

Title: Ga Issues in 3013 Containers

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memorandum

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**SUBJECT: Ga Issues in 3013 Containers: Comments from D.P. Butt,
D. G. Kolman, and M. Stan**

Dave:

Background

According to a recent memo,¹ TSA-10 performed thermal transport calculations that indicated the 3013 high level waste containers could see peak temperatures of in excess of 200°C near the centerline and wall temperatures of approximately 100°C. These containers will be used to hold high level waste for approximately 50 years. My understanding of the 3013 system is that it consists of an outer 316L can, an inner 316 can, and convenience can that is in direct contact with the waste and which is made of 316 with a 416 lid. As I understand it, the outer and inner can have lids welded on, while the 416 lid on the convenience can is threaded. As we've discussed, there are potential issues with the salts and possibly hydrogen in these cans, which we will address separately. However, under the conditions described above, there could also be significant Ga transport to the can walls. Because Ga is known to be a very strong embrittling species, liquid metal embrittlement may be an issue worth investigating further.

In order to assess whether or not this could be an issue, we did a relatively thorough literature survey on Ga embrittlement and performed some preliminary thermodynamic calculations to determine, in particular, potential Ga₂O partial pressures in the can. These results are briefly summarized below.

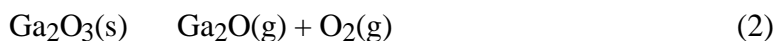
Thermodynamics of Ga evolution

Thermodynamic data for the Pu-Ga-O system were collected and free energies of formation were fit by stepwise multiple linear regression to the equation:

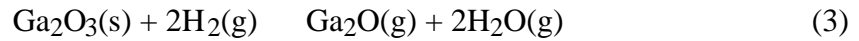
$$G_f = a + bT + cT^{-1} + dT^2 + eT^3 + fT \ln T \quad (1)$$

where $a-f$ are constants, and T is temperature in Kelvin. These data were used to calculate temperature dependent expressions for the vaporization behavior of gallium oxide from a hypothetical waste form. In order to calculate the partial pressure, an activity of Ga or Ga₂O₃ must be assumed since, to my knowledge, they are not known in the actual waste (which contains plutonium oxychloride). However, since Ga is present in weapons grade Pu as a dilute alloying addition of the order of 1 weight percent, it is reasonable and somewhat conservative to assume an activity of 0.01 for the purpose of illustration.

The atmosphere in the container will be He-based, however, there could also be some hydrogen (produced by reactions between water vapor and metal) and perhaps oxychlorides. For the purpose of discussion, we assumed two limiting atmospheres: an inert atmosphere where the gas evolution will be controlled by the mass action, sublimation reaction:



and an atmosphere containing hydrogen where the gas evolution will involve the reduction of gallium oxide by hydrogen according to the mass action reaction:



It should be noted that the species $\text{Ga}_2\text{O}(\text{g})$ may react like a metal because it may be easily reduced by another metal that it contacts, e.g., the wall of the storage container. The partial pressure of Ga_2O , the predominate gas species, can be calculated for equations 2 and 3, respectively, using the relationships:

$$p_{\text{Ga}_2\text{O}} = \frac{a_{\text{Ga}_2\text{O}_3}}{p_{\text{O}_2}} \exp \left[75.69396 - 3.7071 \cdot 10^{-4} T + 2.50277 \cdot 10^{-8} T^2 - \frac{121066}{T} + \frac{117327}{T^2} - 3.82324 \ln T \right] \quad (4)$$

and

$$p_{\text{Ga}_2\text{O}} = \frac{a_{\text{Ga}_2\text{O}_3} p_{\text{H}_2}^2}{p_{\text{H}_2\text{O}}^2} \exp \left[91.3647 + 1.1203 \cdot 10^{-3} T - 7.761944 \cdot 10^{-8} T^2 - \frac{64223}{T} + \frac{157638}{T^2} - 7.8179 \ln T \right] \quad (5)$$

Where a and p represent activity and equilibrium partial pressure, respectively. The equations described above can be used to calculate the equilibrium partial pressures of Ga_2O above, for example, various PuO_x - Ga_2O_3 solid solutions (i.e., assuming various Ga_2O_3 activities) in inert atmospheres or H_2 -bearing gases. Fig. 1, shows how the equilibrium partial pressure varies with environment at a Ga_2O_3 activity of 0.01. It is apparent from this figure, that the vaporization rate under reducing conditions is significantly higher than that in vacuum. It is difficult to say what a significant partial pressure might be. However, it seems reasonable to assume that a partial pressure of 10^{-10} atm might be significant over a period of 50 years. Therefore, these calculations indicate that there is a relatively small window of concern if gaseous evolution of Ga_2O is the controlling phenomenon. If the H_2O content in the cans is kept low, preventing H_2 formation, there could be negligible Ga transport by gaseous diffusion. However, the actual activity of Ga in the waste needs to be determined. Also, these calculations provide a tool for determining the maximum rate of vaporization. The actual rate, which will change with time, must ultimately be determined experimentally.

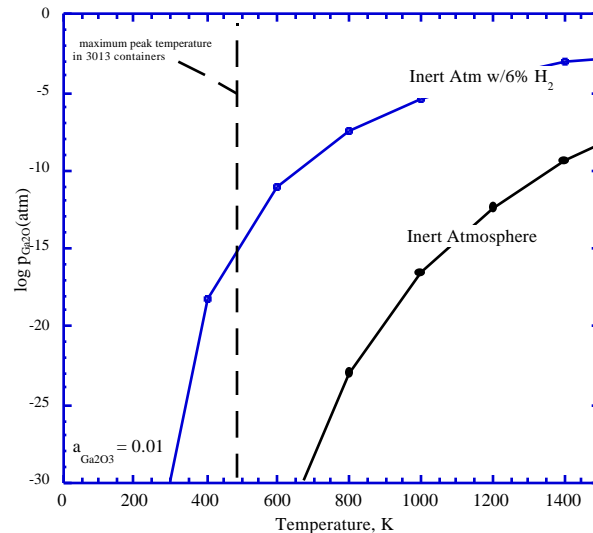
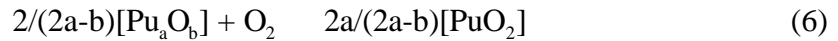


Figure 1. Calculated equilibrium partial pressures above $a_{\text{Ga}_2\text{O}_3} = 0.01$ in helium and a helium-6% H_2 atmosphere.

It is also worth considering the possible form that gallium may have in the waste. If we assume that the gallium is mixed into a PuO_2 -based waste, we can assess whether it is possible that metallic gallium could be present by comparing the standard free energies of oxide formation. Figure 2 shows an Ellingham diagram (left) comparing PuO_2 and $\text{Pu}_{4/3}\text{O}_2$ to Ga_2O_3 , where the data² are normalized, as is conventional, to one mole of oxygen. As the Ellingham diagram indicates, plutonium oxide is thermodynamically more stable than gallium oxide. Thus, plutonium oxide, particularly if substoichiometric in oxygen, could reduce Ga_2O_3 to Ga. However, Besmann^{3,4} suggests (and we agree) that a standard Ellingham diagram does not accurately describe the oxygen potential internal to a solid mixture of PuO_x . He suggests that, because $\text{Pu}_{4/3}\text{O}_2$ and PuO_2 form a solid solution, that the relevant reaction that controls p_{O_2} is most likely:



or, for the more specific condition:



Thus, the oxygen potential should be calculated from the equation:

$$\begin{aligned} RT\ln(p_{\text{O}_2}) \text{ (J/mol)} = & -821,000 + 168.47T - 3RT\ln[(1.5x(1-x/2)^{1/3})/(1-2x)^{4/3}] \\ & - [(3x^2-12x+3)/(1-x/2)^2](63470-49.36T) \end{aligned} \quad (8)$$

where x is the mole fraction of oxygen vacancies, i.e., PuO_{2-x} . Using Besmann's approach we can then calculate an "Ellingham type" diagram (Fig. 2, bottom) comparing the oxygen potential above PuO_{2-x} and Ga_2O_3 . As shown in the figure, at temperatures above approximately 800K (coincidentally near the predicted peak temperature of the 3013 cans), Ga_2O_3 has a more $RT\ln p_{\text{O}_2}$ than $\text{PuO}_{1.99999}$. Thus, Ga_2O_3 is apparently more stable in contact with plutonium oxide at these higher temperatures. However, below approximately 800K, Ga_2O_3 could be reduced Ga (or $\text{Ga}_2\text{O(g)}$). The two diagrams shown in Fig. 2, pose somewhat of a concern (i.e., regardless of which diagram considered, PuO_{2-x} could reduce Ga_2O_3 to Ga at temperatures that can be reached in the 3013 containers), particularly in view of the fact that the melting point of gallium is 30°C. The form of Ga in the actual waste is obviously an issue and should be determined as a function of temperature, atmosphere, and waste type.

Potential for Embrittlement of Stainless Steel

Based on a fairly thorough literature survey, it appears that little information exists on the failure of austenitic stainless steels exposed to Ga. Moreover, the conditions which generated the scant existing information may not be representative of the conditions experienced inside of a can. More specifically, the effects of temperature, radiation, residual stress, humidity, halide concentrations, and weldments, and their potential synergistic effects, have not been studied to our knowledge. Thus, the literature results presented below may or may not be applicable to the specific applications of storage of radioactive waste containing Ga in stainless steel containers.

There are a variety of potential mechanisms whereby gallium can result in failure of austenitic stainless steel materials. They may be generally broken down into 3 categories: liquid metal embrittlement (LME), corrosion by Ga, and alloying by or compound formation with Ga.

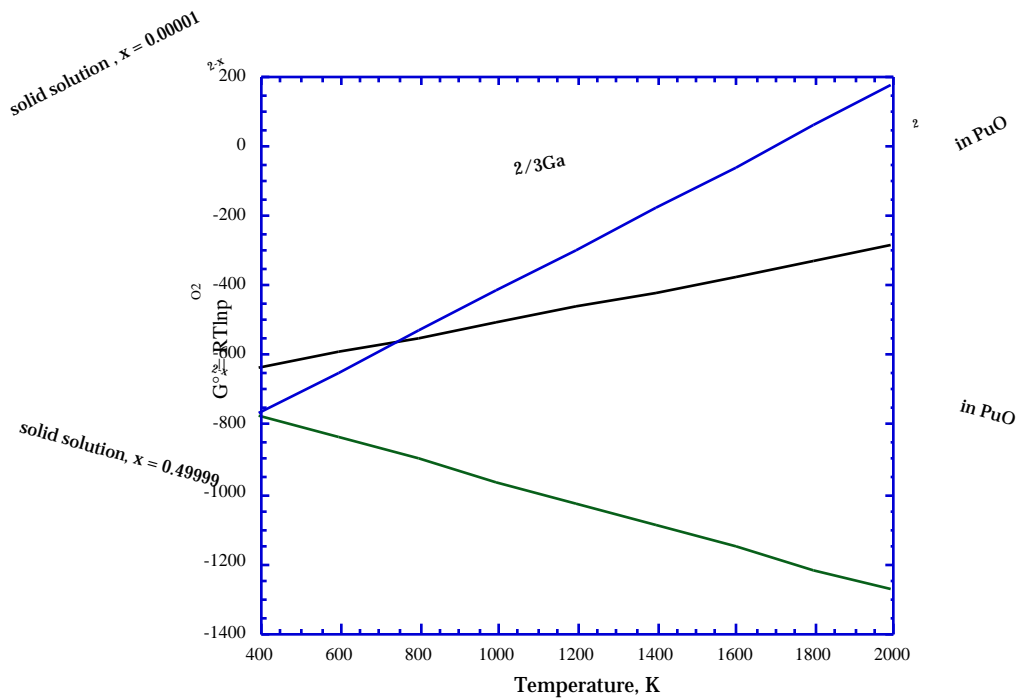
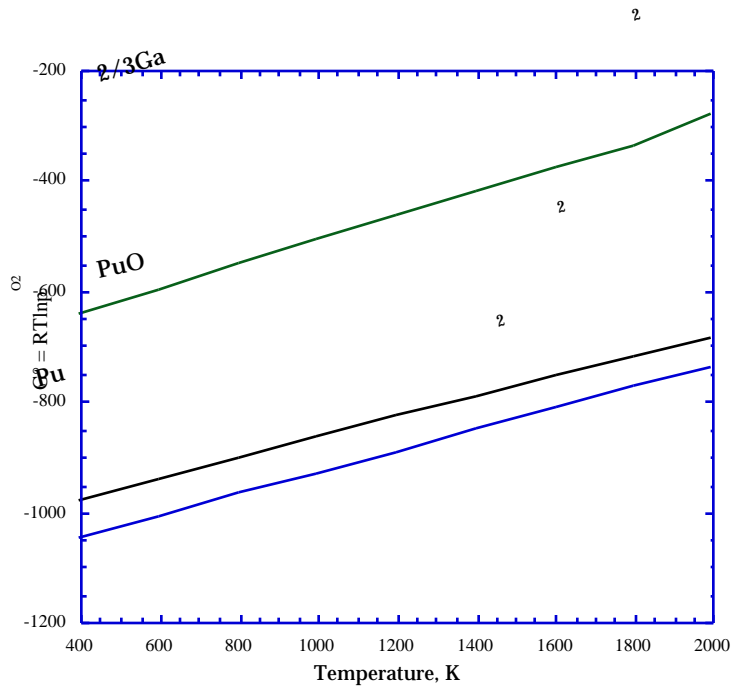


Figure 2. Ellingham diagram (top) comparing the standard free energy of formation of PuO_2 and $\text{Pu}_{4/3}\text{O}_2$ to that of Ga_2O_3 , showing that the plutonium oxides are more thermodynamically stable than Ga_2O_3 . Shown below is an Ellingham type diagram comparing the oxygen potentials above $\text{PuO}_{1.99999}$ and $\text{PuO}_{1.50001}$ to that above Ga_2O_3 according to the method described above. Note that at temperatures below approximately 800K, elemental Ga can be in equilibrium with PuO_2 . Note the two lines at left for PuO_{2-x} represent the range of oxygen potentials above essentially the entire solid solution of $\text{Pu}_{4/3}\text{O}_2$ - PuO_2 .

LME may be defined as a reduction in the failure strength or stress intensity of a material exposed to a liquid metal. LME is not the result of corrosion (i.e., oxidation). Rather it is commonly associated with "the liquid-metal adsorption induced localized reduction in strength of the atomic bonds at the crack tip or at the surface of the solid metal at sites of stress concentrations".⁵ Austenitic stainless steels have been shown to be LM embrittled by Zn ($T > 490^{\circ}\text{C}$). Also, LME by Ga has been shown to be a problem for many materials, most notably Fe - 3 Si^{5,6,7}, Fe^{5,6,8}, some steels^{5,6,9}, aluminum alloys^{5,10,11,12,13} and copper/brass^{5,14,15}. It is unclear whether Ga can LM embrittle austenitic stainless steels. The lack of indication in the literature that Ga LM embrittles stainless steel can tentatively be taken as indication that Ga does not generally LM embrittle stainless steels. However, given the minimal quantity of data, such an assumption is premature.

Little data on the corrosion of austenitic stainless steel by Ga is available. There is some preliminary indication that Ga may be compatible with stainless steels up to 200°C ¹⁶, but this evidence is insufficient to declare the suitability of stainless steel to contain Ga, especially in light of the additional factors pertaining to storage that must be considered (halides, residual stress, weldments, radiation, etc.). Corrosion of stainless steel by oxidized Ga appears to be thermodynamically possible in light of the small heat of formation of oxidized Ga_2O , a potential vapor phase specie. Corrosion pathways include the direct reduction of Ga oxides condensed from the can atmosphere, or in the presence of some humidity, reduction of hydrolyzed Ga species such as HGao_3^{2-} and GaO_2^- in the aqueous surface layer. Either mechanism results in two detrimental effects: oxidation (corrosion) of the stainless steel substrate and production of liquid Ga which is available for LME. Further, because the incorporation of Cr(III) into the oxide on stainless steel is responsible for its passivity, examination of the resistance of Cr to Ga attack can be instructive. Preliminary results suggest that, above 600°C , Cr is not alloyed by Ga but is severely corroded by Ga.¹⁶ Unfortunately, to our knowledge, no data exists on the Ga resistance of Cr at lower temperatures.

Attack of stainless steel by Ga alloying appears possible under certain conditions. Fe has been found to be readily attacked by Ga alloying at all temperatures. Additionally, it has been shown that, above 600°C , stainless steels are subject to severe alloying attack by Ga.¹⁶ As stated above, there is some preliminary indication that Ga may be compatible with stainless steels up to 200°C ,¹⁶ but insufficient evidence exists to judge the suitability of stainless steel for storage of Ga-containing compounds for 50 years.

In summary, little data exists on the resistance of stainless steels to attack by Ga. It has been shown that stainless steels are attacked by Ga at temperatures above 600°C . Although Ga has not been shown to attack stainless steel at temperatures below 200°C , the paucity of data prevents any conclusion as to the resistance of stainless steel to Ga attack at this time. In general, the observation that Ga attacks most materials, including Fe and Cr, by either LME, corrosion, or alloying suggests that attack of stainless steel is plausible. Considering that radiation damage, residual stress, humidity, halides, and weldments are both detrimental to the embrittlement resistance of stainless steel and are present within the container system, stainless steel failure is certainly conceivable, even in the *absence* of Ga. Thus, Ga attack of stainless steels appears probable under some conditions even though there is little data on which to base an informed prediction.

Concluding Remarks

There are insufficient data to determine whether 3013 containers could be susceptible to Ga embrittlement. Likely, the greater concern is the atmospheric effects of chloride (which will be on the order of 20 wt% in the waste) and H_2O combined with radiation effects. However, it would be prudent to have some sound basis to argue whether Ga could be involved significantly in the deterioration of the containers over a 50 year period. My recommendation would be to carry out two parallel studies as a first phase: one looking at the concentrations, activities, and forms of gallium in the waste; and one looking at the susceptibility of stainless steel to Ga embrittlement. The first study could be done by high temperature mass spectroscopy using NMT-6 facilities.

There might need to be some further effort to model the thermodynamics (in simulated can environments) as these measurements progress. The embrittlement studies could be performed in our laboratories. It will be important to do baseline studies of Ga embrittlement as well as studies which look at synergistic effects of Ga with other variables such as [Cl], p_{H_2O} , and radiation. Please let us know if you would like us to act further on this subject.

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1. T. D. Knight and R. G. Steinke, Thermal Analysis of Plutonium Materials in BNFL Containers, Los Alamos National Laboratory Report, Draft-Revision A, April 22, 1997.
 2. I. Barin, Thermochemical Data of Pure Substances, VCH Verlagsgesellschaft, Germany, 1993.
 3. Private Conversations with T. M. Besmann, ORNL, Oak Ridge, TN, May-June, 1997.
 4. T. M. Besmann and T. B. Lindemer, *J. Nucl. Mater.*, **130**, 489 (1985).
 5. M.H. Kamdar in "ASM Handbook, Vol. 11, Failure Analysis and Prevention", ASM International, Metals Park, OH, p. 225 (1986).
 6. M.H. Kamdar in "Treatise on Materials Science and Technology, Volume 25", C.L. Briant and S.K. Banerji eds., Academic Press, London, p. 361 (1983).
 7. M.H. Kamdar, *Prog. Mat. Sci.*, **15**, 289 (1973).
 8. T.M Regand and N.S. Stoloff, *Met. Trans. A*, **8A**, 885 (1977).
 9. M. Tanaka and H. Fukunaga, *J. Soc. Mat. Sci. Jpn.*, **18**, 411 (1969).
 10. B.A. Benson and R.G. Hoagland, *Scr. Metall.*, **23**, 1943 (1989).
 11. S.P. Lynch, *Acta Metal.*, **29**, 325 (1981).
 12. C.F. Old and P. Trevena, *Metal Science*, **13**, 591 (1979).
 13. J.A. Kargol and D.L. Albright, *Met. Trans. A*, **8A**, 27 (1977).
 14. J.T. Lukowski, D.B. Kasul, L.A. Heldt, and C.L. White, *Scr. Metall.*, **24**, 1959 (1990).
 15. P.H. Au-Yeung, J.T. Lukowski, L.A. Heldt, and C.L. White, *Scr. Metall.*, **24**, 95 (1990).
 16. L.R. Kelman, W.D. Wilkinson, and F.L. Yagee in "Resistance of Materials to Attack by Liquid Metals", Argonne National Laboratory Report # ANL-4417 (1950).